WEEKEND/WEEKDAY OZONE OBSERVATIONS IN THE SOUTH COAST AIR BASIN: VOLUME I – EXECUTIVE SUMMARY

FINAL REPORT

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PREFACE

The Desert Research Institute (DRI) and Sonoma Technology, Inc. (STI) conducted a study of the causes of elevated ozone levels on weekends in the South Coast (Los Angeles) Air Basin (SoCAB). This work was conducted over a period of 30 months beginning in December 1999. In the initial phase of the study, DRI examined the spatial, temporal, and statistical distributions of ozone, carbon monoxide, total non-methane hydrocarbons, and nitrogen oxides for routine monitoring sites in the SoCAB with continuous data from 1981 to 1998. STI reviewed available activity data for VOC and NOx emissions and investigated important meteorological phenomena in the SoCAB in the context of day-of-week variations. The results and findings from these retrospective analyses are summarized in the following three volumes:

- Fujita, E.M., W. Stockwell, R.E. Keislar, D.E. Campbell, P.T. Roberts, T.H. Funk, C.P. MacDonald, H.H. Main, and LR. Chinkin (2000a). Weekend/Weekday Ozone Observations in the South Coast Air Basin: Retrospective Analysis of Ambient and Emissions Data and Refinement of Hypotheses, Volume I – Executive Summary. Final report prepared by the Desert Research Institute, Reno, NV and Sonoma Technology, Petaluma, CA for the National Renewable Energy Laboratory, Golden, CO, December 2000.

- Fujita, E.M., W. Stockwell, R.E. Keislar, and D.E. Campbell (2000b). Weekend/Weekday Ozone Observations in the South Coast Air Basin: Retrospective Analysis of Ambient and Emissions Data and Refinement of Hypotheses, Volume II – Desert Research Institute Tasks 1 and 2. Prepared by the Desert Research Institute, Reno, NV for the National Renewable Energy Laboratory, Golden, CO, December 2000.

- Roberts, P.T., T. H. Funk, C.P. MacDonald, H.H. Main, and L.R. Chinkin (2001). Weekend/Weekday Ozone Observations in the South Coast Air Basin: Retrospective Analysis of Ambient and Emissions Data and Refinement of Hypotheses, Volume III – Final report prepared by Sonoma Technology, Inc., Petaluma, CA for the National Renewable Energy Laboratory, Golden, CO, January 2001.

In the second phase of the study, a field measurement program was conducted in September-October 2000 to collect and assemble air quality and emission activity databases to examine relationships between emission patterns and key air quality parameters relevant to the weekend ozone effect. The following interim report presents preliminary results from the field study and describes the applicable measurement methods and approaches for data analysis:

- Fujita, E.M., D.E. Campbell, W. Stockwell, B. Zielinska, J.C. Sagebiel, W. Goliff, M. Keith, and J.L. Bowen (2001). Weekend/Weekday Ozone Observations in the South Coast Air Basin: Phase II Field Study. Interim report prepared by the Desert Research Institute, Reno, NV for the National Renewable Energy Laboratory, Golden, CO, November 2001.

The final report of this study consists of the three volumes referenced below. The Executive Summary (Volume I) provides a synthesis of the results obtained by DRI and STI with respect to a variety of hypotheses for the weekend ozone effect. Volume II documents the results

obtained by DRI from the Phase II field study. It also summarizes the retrospective analyses performed during Phase I and additional analyses that were conducted by DRI to update the findings from Phase I. Volume III is a summary of STI's analysis of the prevailing meteorology during the Phase II field study and their collection of emission activity data in support of this study. Volume III also includes a discussion of weekday/weekend differences in hydrocarbon emissions and ambient concentrations.

- Fujita, E.M., W.R. Stockwell D.E. Campbell, LR. Chinkin, H.H. Main, and P.T. Roberts (2002). Weekend/Weekday Ozone Observations in the South Coast Air Basin Volume I – Executive Summary. Report prepared by the Desert Research Institute, Reno, NV and Sonoma Technology, Petaluma, CA for the National Renewable Energy Laboratory, Golden, CO, and the Coordinating Research Council, May 2002.

- Fujita, E.M., D.E. Campbell, W. Stockwell, R. Keislar, B. Zielinska, J.C. Sagebiel, W. Goliff, M. Keith, and J.L. Bowen (2002). Weekend/Weekday Ozone Observations in the South Coast Air Basin Volume II: Analysis of Air Quality Data. Final report prepared by the Desert Research Institute, Reno, NV for the National Renewable Energy Laboratory, Golden, CO, and the Coordinating Research Council, April 2002.

- Chinkin L.R., H.H. Main, and P.T Roberts. (2002). Weekend/Weekday Ozone Observations in the South Coast Air Basin Volume III: Analysis of Summer 2000 Field Measurements and Supporting Data. Final report prepared by Sonoma Technology, Inc., Petaluma, CA for the National Renewable Energy Laboratory, Golden, CO, April 2002.

ACKNOWLEDGMENTS

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This work was funded by the Department of Energy, Office of Heavy Vehicle Technologies through the National Renewable Energy Laboratory. We gratefully acknowledge the support of Drs. James Eberhardt and Michael Gurevich, of DOE's Office of Heavy Vehicle Technologies for their support. Additional funding was provided by the Coordinating Research Council for the collection and analysis of samples to update source composition profiles for diesel and gasoline exhaust and fuels.

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1. INTRODUCTION

Since the mid 1970's, it has been documented that ozone (O_3) concentrations[1] in the South Coast Air Basin (SoCAB) are higher on weekends than on weekdays, in spite of the fact that emissions of oxides of nitrogen (NOx) and to a lesser extent volatile organic compounds (VOC) [2], are lower on weekends than on weekdays. While ambient ozone levels have decreased substantially throughout the Basin, the magnitude and spatial extent of the weekend effect have become more pronounced, especially during the past decade. In the most recent three-year period with available monitoring data (1998 to 2001), 90 percent of the highest four daily maximum ozone concentrations at air quality monitoring stations from the coastal areas to Riverside occurred on weekends with two-thirds of these highest levels occurring on Sundays. The weekend ozone effect has generated strong interest because of its implications for ozone control strategies. In November 1998, the California Air Resources Board (ARB) adopted the Low Emission Vehicle (LEV-II) regulations, which include significant future NOx emission reductions. The weekend ozone effect was cited at the LEV-II hearing as evidence that further reduction of NOx emissions at this time may be counterproductive for ozone attainment in the SoCAB and other metropolitan areas of the state. At the direction of the Board, ARB Staff conducted a three-year (1999-2002) examination of the weekend effect and the implications of

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[1] Gas-phase species are usually measured as molar ratios (e.g., ppbv or ppmv), which are technically mixing ratios. The term concentration denotes units of mass per unit volume (e.g, $\mu g/m^3$). In common usage, these terms are used interchangeably.

[2] Volatile organic compounds are normally defined as all organic compounds that may be present in the ambient air irrespective of their photochemical reactivity or ability of measurement methods to quantify their concentrations. The following subsets of VOC are used throughout this report. These terms are operational definitions that reflect the sensitivity and selectivity of the analytical methods or photochemical reactivity.

- Non-methane hydrocarbons (NMHC): C_2 through C_{11} hydrocarbons collected in stainless steel canisters and measured by gas chromatography with flame ionization detection (GC-FID) by EPA method TO-14A (U.S. EPA, 1997). Known halocarbons and oxygenated compounds (e.g., aldehydes, ketones, ethers and alcohols) are excluded from NMHC.

- Carbonyls: Aldehydes and ketones, the most common being formaldehyde, acetaldehyde, and acetone. Carbonyls are operationally defined as C_1 through C_7 oxygenated compounds measured by collection on acidified 2,4-dinitrophenylhydrazine (DNPH)-impregnated C18 or silica gel cartridges and analyzed by high performance liquid chromatography with UV detection (HPLC/UV). PAMS carbonyl data normally include only formaldehyde, acetaldehyde, and acetone.

- Non-methane organic compounds (NMOC): Sum of quantifiable peak by EPA Method TO-14A, including unidentified but excluding halocarbons, or by continuous instruments with flame ionization detection. Measured NMOC will be lower for laboratories employing water management. NMOC also refers to the sum of NMHC plus carbonyl compounds by EPA Method TO-11.

- Heavy hydrocarbons: C_{12} through C_{20} hydrocarbons collected on Tenax absorbing substrates and analyzed by thermal desorption and gas chromatography with detection by flame ionization or by mass spectrometry.

- Reactive organic gases (ROG): Organic gases with potential to react with the hydroxyl radical and other chemicals with half-life of <30 days that produce in ozone and secondary organic aerosol. ROG is typically used in reference to inventories of VOC emissions.

NOx reduction as an ozone control strategy. During the same time, the U.S. Department of Energy's Office of Heavy Vehicle Technologies and the Coordinating Research Council also sponsored studies of the weekend ozone effect.

The Desert Research Institute (DRI) and Sonoma Technology, Inc. (STI) conducted a study of the causes of elevated ozone levels on weekends in the South Coast (Los Angeles) Air Basin (SoCAB). This work was conducted over a period of 30 months beginning in December 1999. In Phase I of the study, DRI examined the spatial, temporal, and statistical distributions of ozone, carbon monoxide, total non-methane hydrocarbons, and nitrogen oxides for routine monitoring sites in the SoCAB with continuous data from 1981 to 1998. STI reviewed available emissions activity data, VOC speciation and meteorological phenomena in the SoCAB in the context of day-of-week variations. In Phase II, DRI conducted a nine-day field study in the Los Angeles area from September 30, 2000 to October 8, 2000 to collect and assemble air quality data to examine the relationships between emission patterns and key air quality parameters relevant to the weekend ozone effect. During this field study, STI collected traffic data and determined patterns of emission-related activity at commercial and residential locations near ambient monitors. The key findings of this study are summarized in this Executive Summary (Volume I) according to each of the proposed hypothesis for the weekend ozone effect. Volume II (Fujita et al., 2002) documents the results obtained by DRI from the Phase II field study. It also updates the retrospective analyses performed during Phase I with ambient data for the summer of 1999 and 2000. Volume III (Chinkin et al., 2002) is a summary of STI's analysis of the prevailing meteorology during the Phase II field study and collection of emission activity data in support of this study. Volume III also includes a discussion of weekday/weekend differences in hydrocarbon emissions and ambient concentrations.

1.1 Study Objectives and Hypotheses

The objective of this study was to reconcile the proposed hypotheses for the weekend ozone effect with the fundamentals of ozone photochemistry, historic trends in the magnitude and spatial extent of the weekend effect, and the diurnal and day-of-week variations in the concentrations and source contributions of ozone precursors. During this same time period, Atmospheric Environmental Research, Inc. (AER), ENVIRON, and Envair conducted studies of the weekend ozone effect. During these investigations, the ARB hosted several workshops to provide a forum for exchange of information and results among the investigators conducting research on the weekend ozone effect (information provided at ARB's web site www.arb.ca.gov/aqd/weekendeffect/weekendeffect.htm). These studies were coordinated in that they addressed the following common set of hypothesized explanations of the causes of the effect.

1. **NOx reduction**. Lower concentrations of NOx on weekend mornings lead to higher ozone concentrations on weekends because: a) the accumulation of ozone begins earlier on weekends due to lower nitric oxide (NO) emissions and therefore less titration of ozone with NO; and b) a higher rate of ozone accumulation due to higher VOC/NOx ratios.

2. **NOx timing**. NOx emitted later in the morning and early afternoon on weekends into an aged photochemical system causes these emissions to produce ozone more efficiently compared to the NOx emitted on weekdays.

3. **Pollutant carryover near the ground.** Greater carryover of precursor emissions due to different vehicle activity on Friday and Saturday evening results in increased rate of ozone formation on weekend mornings.

4. **Pollutant carryover aloft.** Carryover of aged pollutants from aloft on weekends has greater influence on weekend mornings due to lower emissions of NOx.

5. **Increased weekend VOC emissions.** Increased VOC emissions from use of lawn and garden equipment, recreational vehicles, backyard barbecues, and household solvents on weekends results in higher weekend ozone concentrations.

6. **Increased photolysis due to decreased emissions of fine particles.** Lower PM concentrations during weekends increase radiation available for photolysis, thus increasing the rate of ozone formation compared to weekdays.

These hypotheses are related to the interactions of ambient concentrations of VOC and NOx, chemical transformations, and transport that affect the day-of-week differences in the diurnal evolution of ozone chemistry. We further hypothesize that the following emission-activity differences between weekdays and weekends are the presumed cause of the air quality effect associated with hypotheses #1, #2, #3, and #6 (relevant hypothesis in parenthesis).

a. Heavy-duty diesel truck (and bus, train) activity is less on weekends during the ozone inhibition (early morning) period than on weekdays resulting in lower NO concentrations and higher VOC/NOx ratios (Hypothesis #1).

b. On-road light-duty gasoline vehicle (LDGV) activity is less on weekends during the ozone inhibition period than on weekdays resulting in lower NO concentrations and less ozone inhibition. VOC emissions from LDGVs are also reduced on weekends, but total reductions in mobile source NOx emissions exceed reductions in VOC emissions resulting in higher VOC/NOx ratios (Hypothesis #1).

c. On-road light-duty gasoline vehicular activity on weekends is similar or higher than weekdays during the ozone accumulation period. Lower diesel NOx emissions during the same period result in higher weekend VOC/NOx ratios during this period (Hypothesis #1 and 2).

d. Heavy-duty diesel activity is decreased on Friday and Saturday evenings compared to other evenings resulting in overnight carryover of pollutants with higher VOC/NOx ratios (Hypothesis #3).

e. Light-duty gasoline vehicle traffic is increased while heavy-duty diesel traffic is decreased on Friday and Saturday evenings compared to other evenings resulting in overnight carryover of pollutants with higher VOC/NOx ratios (Hypothesis #3).

f. Lower vehicle traffic on weekends, especially heavy-duty diesel truck (and bus, train), results in lower direct emissions of soot particles that absorb light (Hypothesis #6).

DRI addressed all of the above hypotheses except #4 and STI addressed each hypothesis except #6. Both groups addressed each emission hypothesis to varying degrees and by complementary approaches – DRI used ambient data while STI used emission activity data. The work performed by DRI and STI is documented separately in Volumes II and III of this report, respectively, and is integrated and synthesized in this Executive Summary (Volume I).

1.2 Study Scope and Approach

In Phase I of the study (Fujita et al., 2000b), DRI examined historic trends in the average daily maximum hour ozone in the SoCAB from 1981 to 1998 and the evolution of the magnitude and spatial extent of the weekend ozone effect over this period. Monitoring sites include N. Long Beach, Anaheim, Lynwood, Los Angeles–North Main, Reseda, Burbank, Pico Rivera, La Habra; Azusa, Pomona, Upland, and Rubidoux. The ozone trends were associated with day-of-week variations in the diurnal behavior of ozone, NO, nitrogen dioxide (NO_2), and carbon monoxide (CO), which serves as an estimate of nonmethane hydrocarbons (NMHC). The retrospective analysis of ambient data focused on day-of-week differences in the overnight carryover of ozone precursors, the extent of inhibition of ozone formation during the morning due to titration with NO, and the rate of ozone accumulation from the end of the inhibition period to time of peak ozone. For the purposes of this analysis, the time at which the declining concentration of NO matched the rising concentration of O_3 was used to mark the end of the ozone inhibition period and the start of ozone accumulation. Changes in the rate of ozone accumulation were correlated to historic trends in CO/NOx ratios, which served as partial surrogates for trends in VOC/NOx ratios.

As part of Phase I, STI evaluated emissions, meteorological and ozone aloft data to better understand the weekend ozone phenomena (Roberts et al., 2001). STI examined the degree to which aloft ozone influences surface ozone concentrations. Previous analyses of aloft ozone data from 1987 Southern California Air Quality Study (SCAQS) have shown the presence of deep layers (about 500 m) of high ozone concentrations over a wide portion of the SoCAB (e.g., Roberts and Main, 1992). The aloft ozone can contribute to the surface ozone concentrations when mixed to the surface during the day. During the 1997 Southern California Ozone Study (SCOS97-NARSTO) a Lidar located at El Monte (EMT) collected aloft ozone data from 90 m above ground level (agl) to about 2500 m agl during intensive operational periods (IOPs). Aloft wind and mixing height data were also collected at EMT. These data were used to examine the variability of the characteristics of these aloft ozone layers during ozone episodes and the influences of mixing heights and wind patterns on ozone concentrations. The emissions-related objectives of this study were twofold: 1) to develop a comprehensive, priority listing of emissions-related hypotheses for further study; and 2) to identify existing sources of emissions data and assess the feasibility of gathering adequate data to refute or support each hypothesis.

In Phase II of the study, a field measurement program was conducted from September 30, 2000 to October 8, 2000 to collect and assemble air quality and emission activity databases to examine relationships between emission patterns and key air quality parameters relevant to the weekend ozone effect. The ambient air quality measurements by DRI involved supplemental

measurements at existing South Coast Air Quality Management District (SCAQMD) monitoring sites and mobile sampling along freeway and surface street loops and at regional/background sites (see Figure 1). Supplemental measurements included hourly speciated C_2 to C_{11} volatile organic compounds by automated gas chromatography with mass spectrometry at Azusa, continuous black carbon by light absorption at Azusa and Pico Rivera, and 3-hour composite Tenax samples for C_8 to C_{18} hydrocarbons at Azusa and Pico Rivera beginning at 2, 6, and 9 a.m. PDT. ARB also collected canister samples at Los Angeles–North Main for speciated hydrocarbons on the same schedule, and SCAQMD measured 3-hour average speciated VOC with an automated gas chromatograph at Pico Rivera. Carbon monoxide, NO, reactive oxidized nitrogen (NOy)[3], black carbon and speciated hydrocarbons were measured simultaneously in a mobile van during four weekend days (two Saturdays and two Sundays) and one day each during Monday, Wednesday, and Friday. Measurements were made during the carryover period (2-5 a.m. PDT) at the Industry Hills Conference Center (IH1–see Figure 1), Covina freeway loop (CV1), Dodger Stadium (DS1), and Compton freeway loop (CO1), during the ozone inhibition period (6-9 a.m.) at Dodger Stadium (DS2) and Compton freeway loop (CO2); and during the ozone accumulation period (9 a.m. to noon) at Covina freeway loop (CV2), Industry Hills (IH2), and the Pomona freeway loop (PO1).

The time series of NO, NOx and CO were related to indicators of compression-ignition exhaust (black carbon and heavy hydrocarbons) and spark-ignition exhaust [CO and methyl tertiary-butyl ether (MTBE)] by time of day and day of week. DRI used multiple regression analysis to estimate the amounts of NOx associated with CO and MTBE relative to the NOx associated with black carbon and nC_{10}-nC_{15}. Diurnal and day-of-week variations in the associations of NOx to pollutants were correlated to the relative contributions of diesel and gasoline exhaust to ambient NOx. The source contributions of gasoline engine and diesel engine exhaust to NMHC and NOx were estimated by Chemical Mass Balance (CMB) receptor modeling using source composition profiles that were derived for diesel and gasoline exhaust from samples collected at a truck stop and on a stretch of the 110 Freeway where heavy trucks are prohibited. Source profiles were also developed from analysis of gasoline and diesel fuel samples. In addition to the relative contributions of gasoline and diesel exhaust, the detailed speciation of VOC from the mobile sampling and the time-resolved VOC speciation at Los Angeles, Azusa, and Pico Rivera monitoring stations provided source attribution of other sources of VOC by time of day and day of week. These analyses address questions regarding the source contributions of VOC carried over from the previous evening and the relative importance of on-road versus other area sources in the diurnal variations in VOC/NOx ratios. Diurnal variations in VOC composition were also used to examine day-of-week differences in ozone formation potential and reactivity of the VOC mix. To aid in interpretation of the ambient data, STI examined the day-to-day differences in meteorology that could have affected ozone precursors and emissions activities during the field study period. STI also evaluated which weekend days

[3] Reactive oxidized nitrogen (NOy) includes nitric oxide (NO), nitrogen dioxide (NO_2), peroxyacetyl nitrate (PAN) and other PAN analogues, nitric acid (HNO_3), nitrate aerosol (NO_3^-), nitrous acid (HONO), peroxynitric acid (HNO_4), nitrate radical (NO_3), dinitrogen pentoxide (N_2O_5), and organic nitrates.

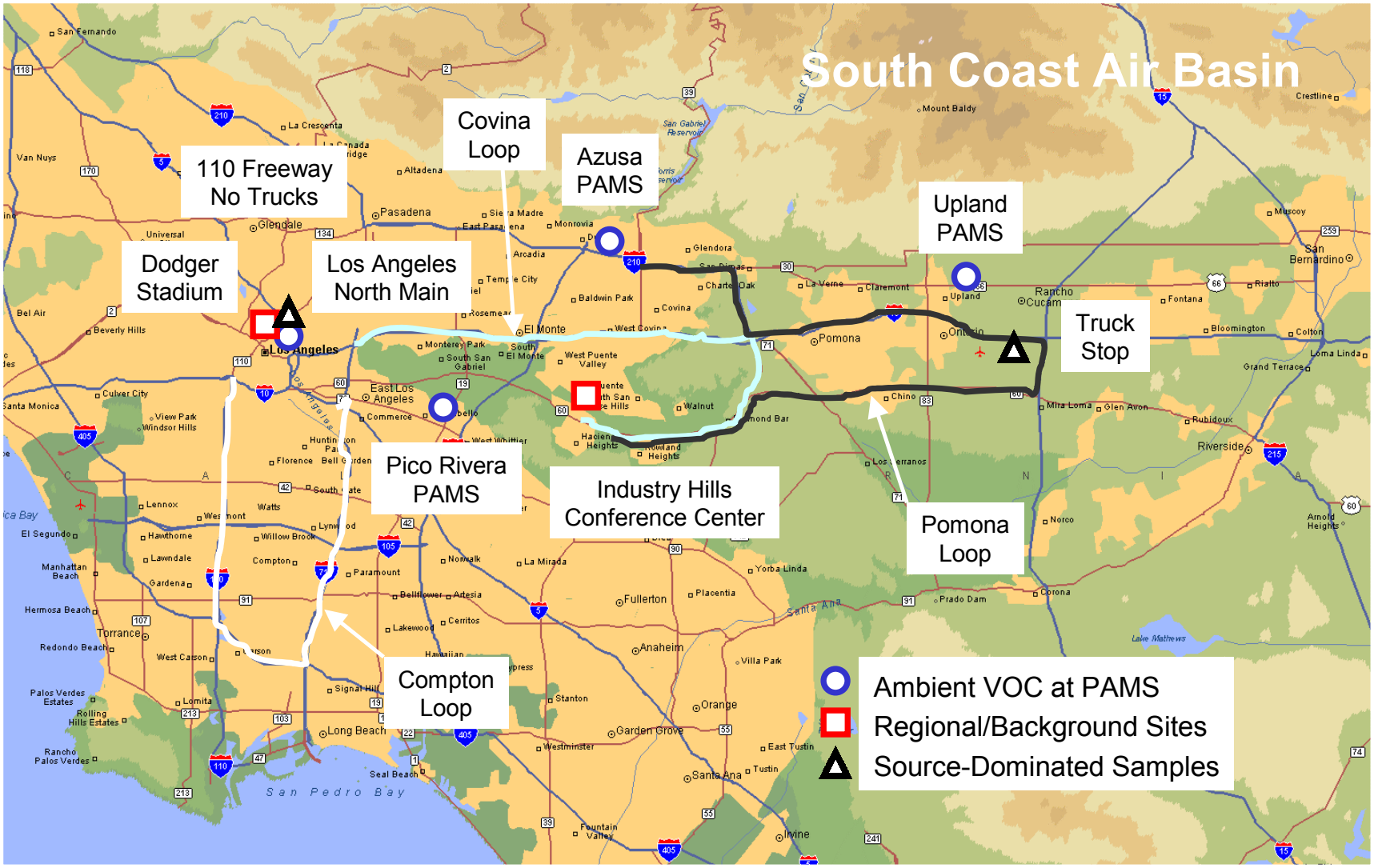

Figure 1-1. Map of the South Coast Air Basin showing the location of the Pico Rivera, Azusa, and Upland PAMS sites, the Los Angeles North Main monitoring station, and the three freeway loops and two regional/background sites used during the September 30 to October 8, 2000 field study.

were meteorologically similar to which weekdays to allow a comparison of emission and ozone precursor concentrations on identified days independent of meteorology.

Also as part of Phase II, STI evaluated various emissions-related activities for both the entire summer period and the field study period. These evaluations covered prevailing meteorology, surface street and freeway traffic data, and patterns of emission-related activity at commercial and residential locations near ambient monitors by day-of-week. For sources identified in Phase I as having a significant potential difference in weekday and weekend emissions, a data collection effort was undertaken to acquire relevant weekday and weekend activity data. Specifically, new emissions activity data were collected for on-road mobile sources, lawn and garden equipment sources, selected area-wide sources, and major point sources in the SoCAB. Surveys of land use and emissions source types near selected air quality monitoring sites were also conducted.

DRI updated the retrospective analyses from Phase I by examining the summer 1999 and 2000 ambient data from the Photochemical Assessment Monitoring Stations (PAMS) at Azusa, Pico Rivera, and Upland and from the California Air Resources Board ozone precursor trends site in downtown Los Angeles (North Main) (Fujita et al., 2002b). These analyses focused on relating weekday differences in the diurnal variations of CO, NMHC, NO, and NO_2, and NOx with variations in ozone, VOC/NOx ratios, and the ratios of O_3 to potential ozone (i.e., O_3 plus NOx). Day-of-week variations in ozone concentrations were also related to VOC reactivity, photochemical aging, and the estimated photolysis rate parameter for NO_2. The Regional Atmospheric Chemical Mechanism (RACM; Stockwell et al., 1990) was used in a chemical box model to calculate ozone isopleths from initial concentrations of VOC determined from measured VOC concentrations obtained between 6-9 a.m. Current weekday and weekend observations of the VOC and NOx mixing ratios were superimposed on the ozone isopleth plot along with similar observations from 1987.

2. SUMMARY OF RESULTS

Southern California has historically experienced the most severe ozone pollution in the United States. Prior to the implementation of emission reduction measures, hourly averaged ozone concentrations approaching 0.70 ppm were reported in the South Coast Air Basin (SoCAB), and Stage III episodes (ozone exceeding 0.50 ppm) were relatively frequent events in the 1960s. Because of three decades of progressively more stringent emission controls, the frequency and intensity of excessive ozone concentrations in the SoCAB have been significantly reduced. The Basin recorded 167 days exceeding the National Ambient Air Quality Standard (NAAQS) of 0.12 ppm maximum hourly average for ozone in 1980, 158 days in 1985, 130 days in 1990, 98 days in 1995 and 33 days in 2000 (SCAQMD, 2001). The maximum hourly average concentrations of ozone in the Basin declined during this twenty-year period from 0.45 ppm to 0.18 ppm.

2.1 Evolution of the Weekend Ozone Effect in the South Coast Air Basin

While peak levels of ozone have dropped sharply in the SoCAB, the highest levels of ozone now occur more frequently on Sundays throughout the Basin. Figure 2-1 shows that in the period 1981-84, peak ozone levels were higher on weekdays in most of the central and eastern portions of the Basin. Most monitoring sites in the western Basin showed slightly higher weekend ozone concentrations. By 1990-94, ozone concentrations were higher on weekends throughout the Basin and the weekend effect continued to strengthen after 1995. The twelve-site average Sunday/Wednesday ratios in peak ozone for the periods 1981-84, 1985-89, 1990-94, and 1995-98 are 1.00, 1.02, 1.18 and 1.26, respectively. The corresponding Saturday/Wednesday ratios are 1.03, 1.04, 1.17, and 1.24, respectively. Ozone concentrations in 1995-98 expressed as ratios of the 1981-84 values range from 0.54 to 0.59 for weekdays (Monday through Friday), 0.67 on Saturday, and 0.70 on Sunday. The larger reductions in peak ozone concentrations on weekdays were accompanied by a shift in the location of peak ozone levels from the central portion of the Basin to the eastern Basin and mountain locations. In the western Basin, represented by Los Angeles – North Main, the current (1999-2000) mean peak ozone levels are about 60 ppb lower than in 1980-85 for all days of the week. In contrast, decreases in peak ozone in the central Basin (Azusa and Upland) have been greater on weekdays (~ 100 to 110 ppb) than on Saturdays (~ 70 to 90 ppb) or Sundays (60 to 70 ppb).

The current weekend ozone effect in the SoCAB is illustrated by the correlations in Figure 2-2 of the summer 1999-2000 mean hourly ozone and NO concentrations during the daylight hours (6:00 a.m. to 9:00 pm) at Azusa during midweek (Tuesday to Thursday) versus the corresponding hourly pollutant concentrations on Monday, Friday, Saturday, and Sunday. NO is lower on weekends relative to midweek by about the same ratio for all daylight hours. Conversely, ozone is higher on weekends relative to midweek by a constant ratio for all daylight hours. The corresponding plots for Los Angeles – North Main, Pico Rivera, and Upland (not shown) show similar correlations. The Saturday/midweek ratios for ozone during the daylight hours ranged from 1.26 to 1.31 at the four sites with a mean of 1.28. The corresponding ratios for NO ranged from 0.51 to 0.69 with a mean of 0.61. The Sunday/midweek ratios for ozone during daylight hours ranged from 1.44 to 1.55 with a mean of 1.50. The ratios for NO ranged from 0.29

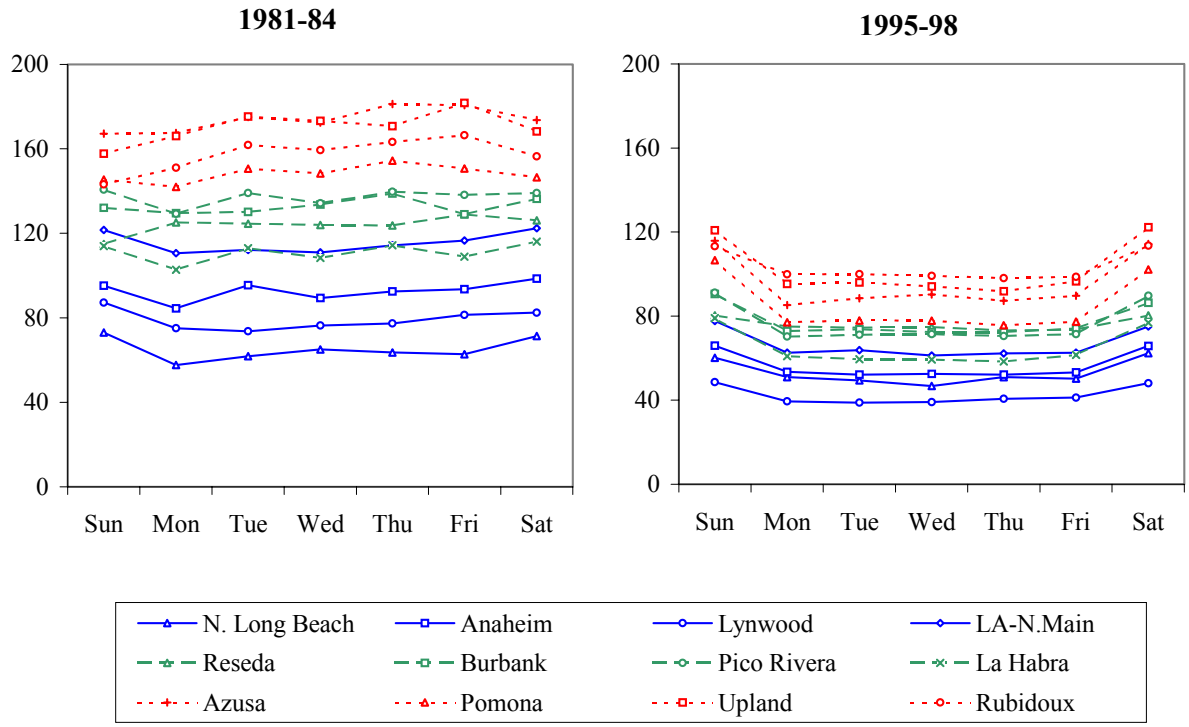

Figure 2-1. Mean maximum 1-hour concentrations (ppb) of ozone during summers (June 1 to September 30) of 1981-1984 and 1995 to 1998 in the South Coast Air Basin. Sites in the western, northern and central, and central to eastern basin are denoted by solid, dash, and dotted lines, respectively

to 0.43 with a mean of 0.35. The correlations are extremely good with R^2s of 0.98 or better. As expected, correlations of the midweek hourly NO and O_3 mixing ratios with the corresponding hourly values on Monday and Friday show little variance with one another. These results indicate that each of the sites we examined has its own relative ozone pattern that is fixed for all days of the week and that what differentiates weekday from weekend is a multiplicative constant. These results suggest that the weekday-weekend differences in the diurnal pattern of NO and ozone are established early in the morning, and the influence of the chemical factors (either emissions and/or rate and efficiency of ozone formation) related to this "constant" is maintained throughout the daylight hours.

2.2 Emissions and Relationship to Weekend and Weekday Concentrations

The estimates of average summer 2000 emissions in the SoCAB are listed in Table 2-1 by source category (stationary and area, on-road mobile, and other mobile), pollutant, and subcategory (e.g., gasoline and diesel vehicles). On-road mobile source emissions estimates are derived by the ARB using EMFAC2000 Version 2.02. Table 2-2 shows that on-road mobile sources are the single largest source category for ozone precursor pollutants, accounting for 49%, 62%, and 80% of average daily ROG, NO_x, and CO, respectively, in the SoCAB. Most of the

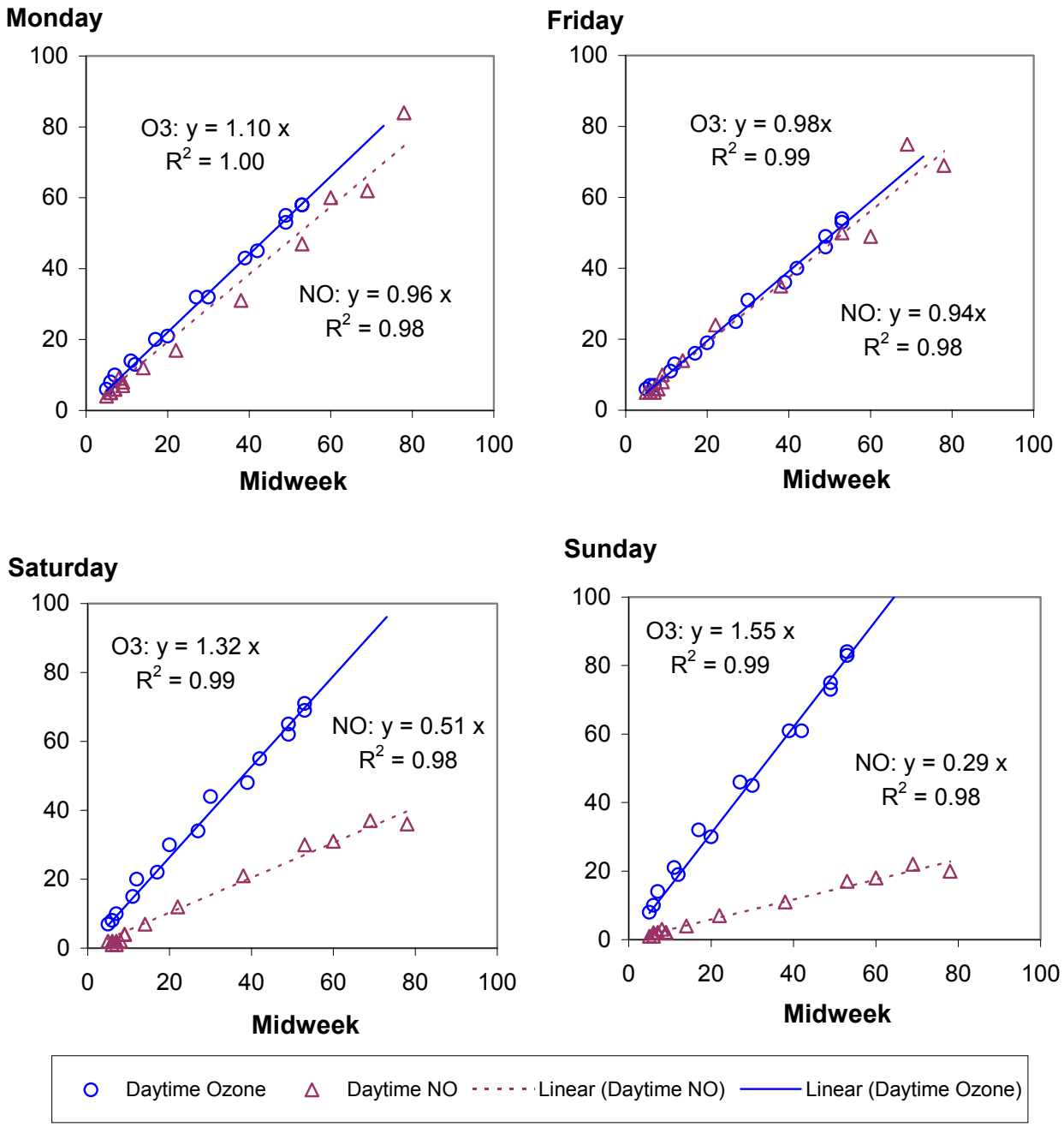

Figure 2-2. Correlation plots of summer 1999-2000 mean hourly ozone and NO mixing ratios at Azusa during midweek (Tues-Thur) versus Monday, Friday, Saturday, and Sunday for daylight (6:00 a.m. – 9:00 p.m.) hours.

Table 2-1. Estimated average summertime emissions for 2000 in the SoCAB (tons/day).

Source Category	ROG	NO_x	CO	PM_{10}
Stationary and Area Sources				
Fuel Combustion	12	87	43	8
Waste Disposal	3	2	1	0
Cleaning & Surface Coatings (Industrial)	137	0	0	0
Petroleum Production & Marketing	37	4	5	1
Industrial Processes	23	11	6	13
Solvent Evaporation (Consumer)	182	0	0	0
Misc. Processes (Residential Fuel Combustion, Road Dust)	16	24	83	284
Total, Stationary and Area Sources	**409**	**128**	**137**	**307**
On-Road Mobile Sources				
Passenger Cars	323	247	2990	9
Light- & Medium-Duty Trucks	160	192	1896	8
Light-, Medium-, & Heavy-Duty Trucks (Gasoline)	46	56	622	6
Light-, Medium-, & Heavy-Duty Trucks (Diesel)	13	227	62	8
Other On-Road Mobile	10	1	106	2
Source Category	ROG	NO_x	CO	PM_{10}
Other Mobile Sources (Off-road equipment)	155	313	1250	20
Total, On- and Off-road Mobile Sources	**706**	**1037**	**6927**	**54**
Total (all anthropogenic categories)	**1115**	**1165**	**7064**	**360**
Total (all biogenic categories)[1]	**125**	**–**	**–**	**–**

[1] Note that current estimates of biogenic hydrocarbon emissions are uncertain. Benjamin et al. (1997) estimate present biogenic hydrocarbon emissions of 125 to 200 TPD. However, "Since the majority of the biogenic hydrocarbon emissions occur in the mountains located on the northern and eastern boundaries of the SoCAB, downwind of the most heavily populated areas, the actual impact of these emissions on air quality is probably less than is suggested by the magnitude of the inventory, even after taking into account the higher reactivity of the vegetative hydrocarbons." Source of table: CARB web site: http://www.arb.ca.gov/app/emsinv/fcemssumcat.html December, 2001.

Table 2-2. Estimated average daily emissions by major source category for summer 2000 in the SoCAB (percent of total).

Source Category	ROG	NO_x	CO	PM_{10}
Stationary & Area-Wide	37	11	2	85
On-road Mobile	49	62	80	9
Other Mobile	14	27	18	6

on-road emissions are due to gasoline vehicles, but diesel vehicles contribute substantially to NO_x emissions. Following on-road mobile sources, stationary and area-wide sources are significant sources of ROG, while other mobile sources are a less important source of ROG. In contrast, other mobile sources generate relatively large emissions of NO_x, while stationary and area-wide sources are less important NO_x contributors. The majority of CO emissions are associated with on-road and other mobile sources. While CO emissions are not a major contributor to ozone formation, CO serves as a tracer for mobile source emissions because CO is associated primarily with mobile source fuel combustion.

Average relative traffic volumes by day of week and hour of day are shown in Figures 2-3 through 2-5. Passenger-type vehicles (including cars, pickup trucks, SUVs, vans, and motorcycles) account for about 85-95% of the total traffic volume at every location where vehicle classes were monitored. Figure 2-3 shows the day-of-week patterns in total traffic volumes. The average weekday represents about 15% of total weekly traffic counts and the average weekend day represents about 12-13% of total weekly traffic counts. This represents a drop of 13-20% in total daily travel activity on weekend days relative to weekdays. In addition, diurnal patterns of travel activity differed between weekends and weekdays (see Figure 2-4). On weekdays, bimodal distributions were observed with peaks in activity corresponding to the morning and afternoon rush hours around 0730 and 1700 PDT. On weekends, single-mode distributions were observed with broad peaks in activity centered around 1330 PDT. Further analyses show that distinct traffic patterns also exist between Saturday and Sunday. Figures 2-5a and 2-5b show that total daily surface street travel activity for trucks dropped 44-67% on weekends. Note that heavy-duty truck traffic is the only on-road category that showed a different pattern of activity on freeways relative to surface streets. Heavy-duty traffic has a single peak in activity on freeways and a dual-mode peak in traffic activity on surface streets; all other on-road categories have surface street activity similar to freeway traffic. Using the day-of-week activity patterns developed in this study, the resulting emissions for year 2000 are depicted in Figure 2-6.

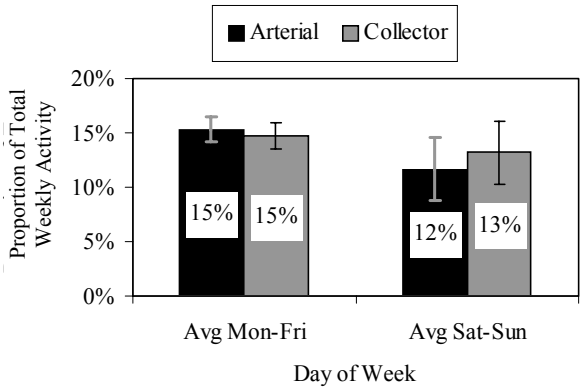

Figure 2-3. Average day-of-week traffic patterns observed for surface streets. Error bars bound 1 standard deviation.

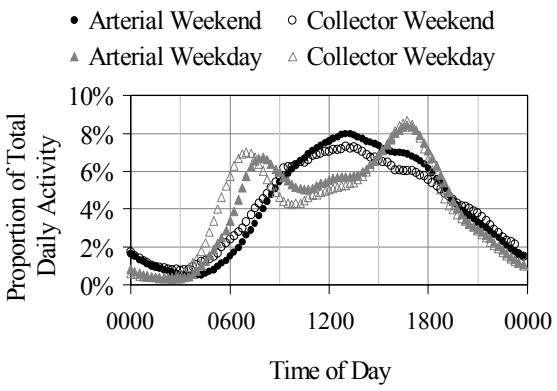

Figure 2-4. Average diurnal traffic patterns observed for surface streets.

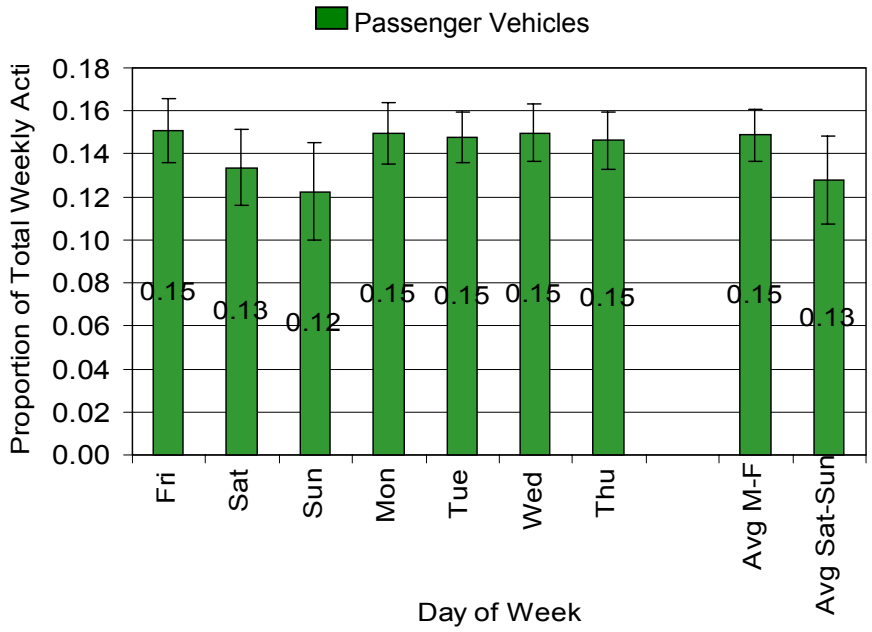

Figure 2-5a. Average day-of-week traffic patterns observed for passenger vehicles and medium-duty trucks on surface streets. Error bars bound 1 standard deviation.

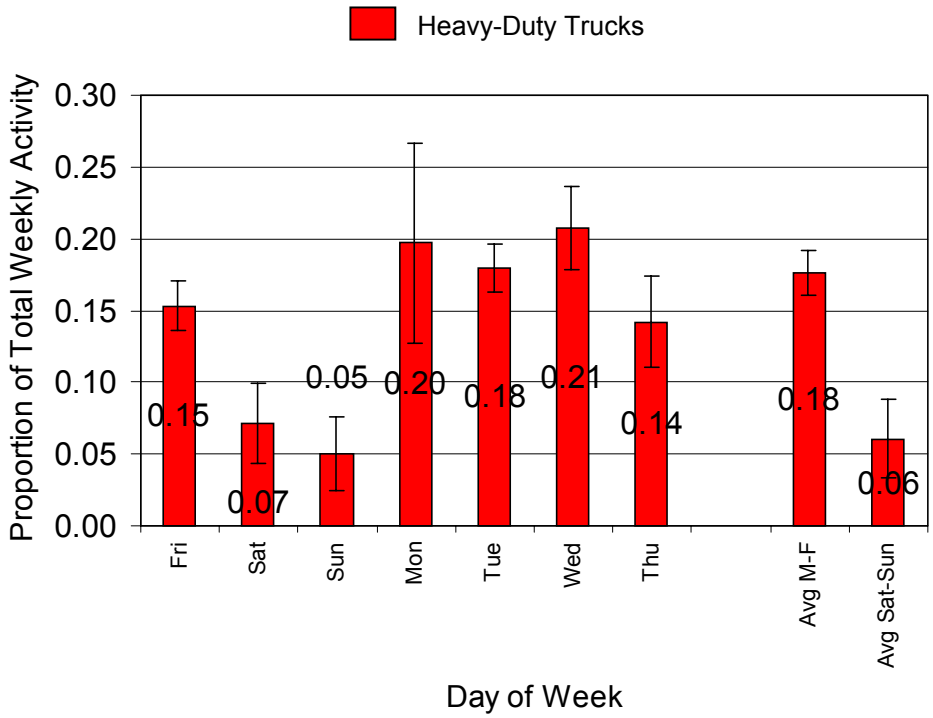

Figure 2-5b. Average day-of-week traffic patterns observed for heavy-duty trucks and buses on surface streets. Error bars bound 1 standard deviation.

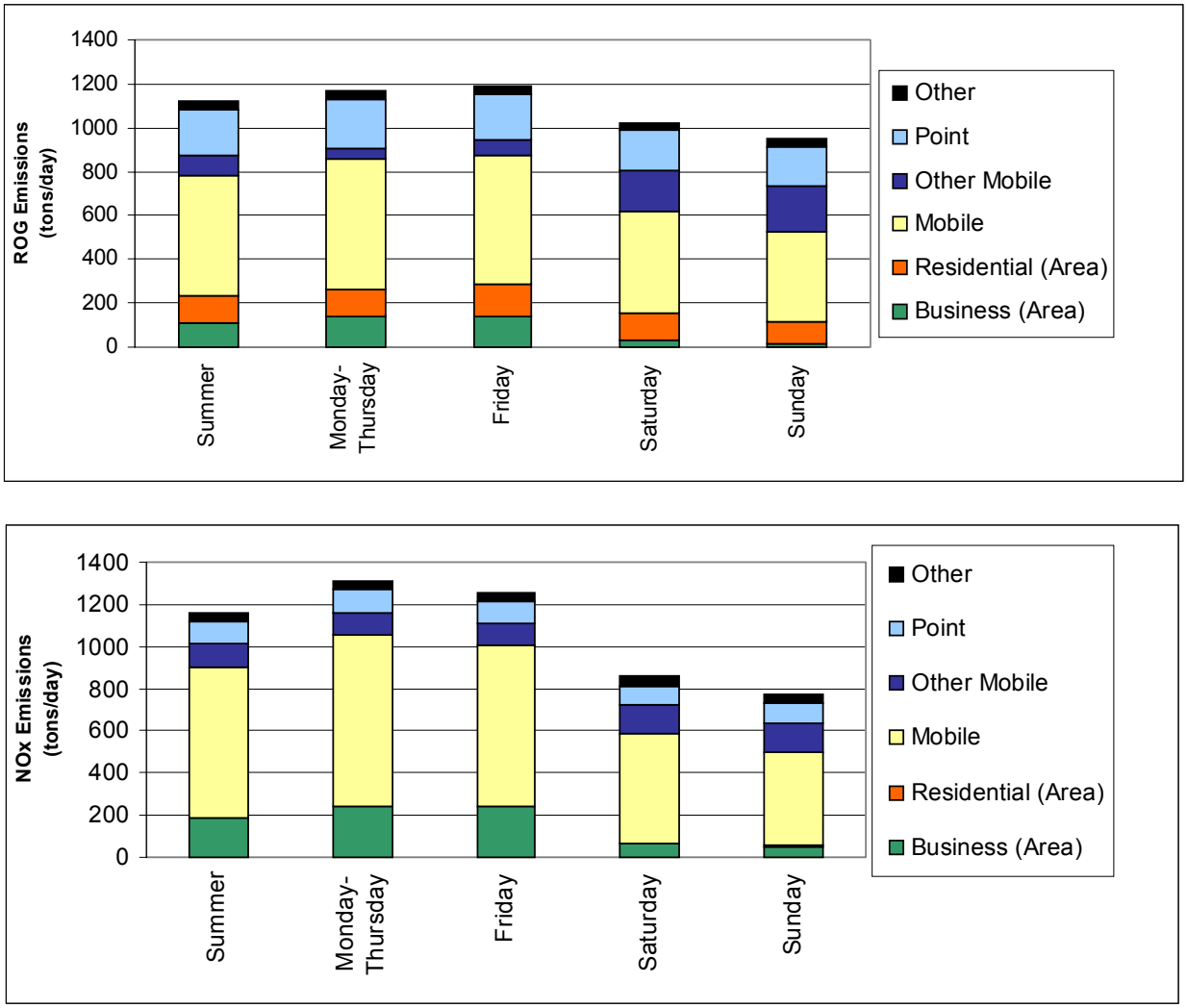

Figure 2-6. Estimated 2000 day-of-week emissions in the SoCAB.

2.3 Conceptual Explanation of Weekend Ozone Effect in the South Coast Air Basin

The weekend ozone effect is rooted in ozone's complex photochemistry in which the rate of O_3 formation is a nonlinear function of the mixture of VOC and NOx in the atmosphere. Depending upon the relative concentrations of VOC and NOx and the specific mix of VOC present, the rate of O_3 formation can be more sensitive to changes in VOC alone or to changes in NOx alone or to simultaneous changes in both VOC and NOx. Ozone is produced in the atmosphere by the reaction of an oxygen atom (O) and molecular oxygen (O_2). At lower altitudes, the photodissociation of nitrogen dioxide (NO_2) into nitric oxide (NO) and atomic oxygen is the only significant source of oxygen atom. The oxygen atom reacts with O_2 to produce O_3. However, NO reacts rapidly with O_3 to regenerate NO_2. The reactions occur rapidly, establishing a steady-state equilibrium ozone concentration [O_3] that is determined by the following "NO-photostationary state equation,"

$$[O_3] = \frac{J_1[NO_2]}{k_3[NO]}$$

where J_1 is the photolysis frequency of NO_2 to NO and O, k_3 is the rate constant for the reaction of O_3 with NO, $[NO_2]$ is the concentration of nitrogen dioxide, and [NO] is the concentration of nitric oxide. Because these reactions only recycle O_3 and NO_x, they are insufficient, by themselves, to create excessive ozone levels. When volatile organic compounds are present, however, their oxidation produces the hydroperoxy radical (HO_2) and organic peroxy radicals (RO_2), which react with NO to form NO_2 without destruction of ozone, thereby allowing ozone to accumulate by increasing the ratio of $[NO_2]$ to [NO].

The hydroxyl radical (HO) initiates the oxidation of VOCs that form the peroxy radicals. VOCs are consumed in the sequence of ozone formation, while HO, HO_2, and NOx act as catalysts. Termination occurs by reaction of HO with NO_2 to form nitric acid (HNO_3) or when HO_2 combines to form hydrogen peroxide (H_2O_2). The production efficiency of O_3 per molecule of NOx varies with total concentration of NOx and the ratio of VOC to NOx. At low VOC-to-NO_2 ratios, HO reacts predominantly with NO_2, removing radicals and retarding O_3 formation. Under these conditions, a decrease in NOx concentration favors O_3 formation. High ratios of VOC to NOx concentration favor HO reaction with VOCs that generate new radicals that accelerate O_3 production. At a sufficiently low concentration of NOx, or a sufficiently high VOC-to-NO_2 ratio, a further decrease in NOx favors peroxy radical-peroxy radical reactions, which retard O_3 formation by removing free radicals from the system. At a given level of VOC, there exists a NOx mixing ratio at which a maximum amount of ozone is produced. This optimum VOC/NOx ratio depends upon the reactivity to HO of the particular mix of VOCs that are present. For ratios less than this optimum ratio, increasing NOx decreases ozone.

The ozone isopleth diagram shown in Figure 2-7 illustrates the dependence of O_3 production on the initial amounts of VOC and NOx. The ozone ridge in the isopleth diagrams corresponds to the maximum O_3 concentration that can be achieved at a given VOC level. The VOC/NOx ratio at the ridgeline is about 10 to 12. The HO radical chain length, which is the number of times a newly formed HO radical is regenerated through radical chain propagation before it is destroyed, reaches a maximum at this VOC/NOx ratio. Thus, the ridgeline corresponds to the VOC/NOx ratio at which O_3 is most efficiently formed. Above the ridgeline, a reduction of NOx lowers the rate at which HO and NO_2 are removed by formation of HNO_3 and leads to an increase in maximum O_3. This region is commonly described as "VOC-limited" (i.e., lowering VOC most effectively reduces O_3). "NOx-disbenefit" refers to a situation when NOx reduction leads to an increase in ozone. This disbenefit occurs only in the VOC-limited region. Below the ridgeline at low NOx concentrations, there is a large region where lowering NOx most effectively reduces O_3 and large reductions in VOC have practically no effect on maximum O_3.

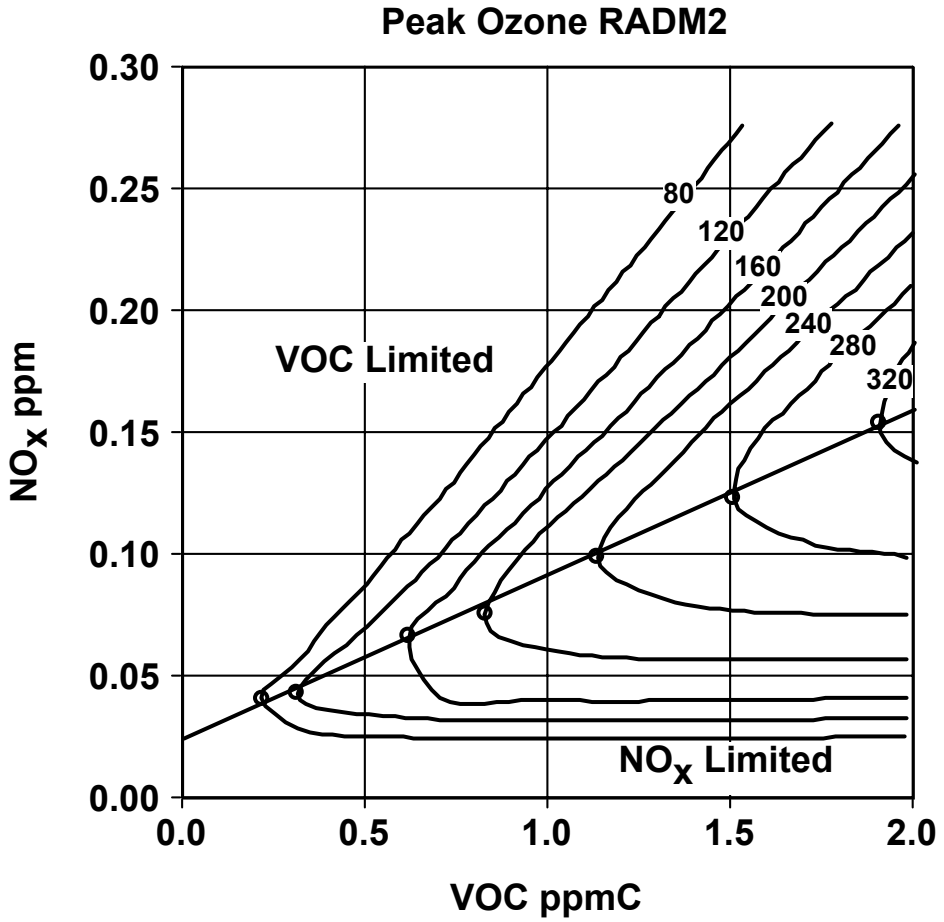

Figure 2-7. Typical ozone isopleth plot showing 1-hour maximum ozone concentrations (in ppb) calculated as a function of initial VOC and NOx concentrations and the regions of the diagram that are characterized as VOC- or NOx-limited. The ozone isopleth plot was generated using the Ozone Isopleth Plotting Program, Research Version (OZIPR) with the RADM2 chemical mechanism (Stockwell et al. 1990).

This region is described as "NOx-limited". A decrease in NOx above the ridgeline increases ozone while a decrease in NOx below the ridgeline decreases ozone.

NO typically exists in excess of O_3 in the urban center overnight, and suppresses the concentration of O_3 to zero or near zero in the surface layer. Fresh NO emissions during the morning commute prolong the inhibition of ozone accumulation after sunrise. During this inhibition period, the photolysis of carbonyl compounds and smaller contributions of nitrous acid (HONO) and other radical precursors are the primary source of HO radicals until a sufficient amount of NO has been converted to NO_2. O_3 carried over aloft from the previous day can mix down in the morning and contribute O_3 and radicals to the developing surface ozone chemistry. The length of the morning ozone inhibition period is largely determined by the concentration of NO and NO_2/NOx ratios. Figure 2-8 shows the average weekday versus weekend diurnal

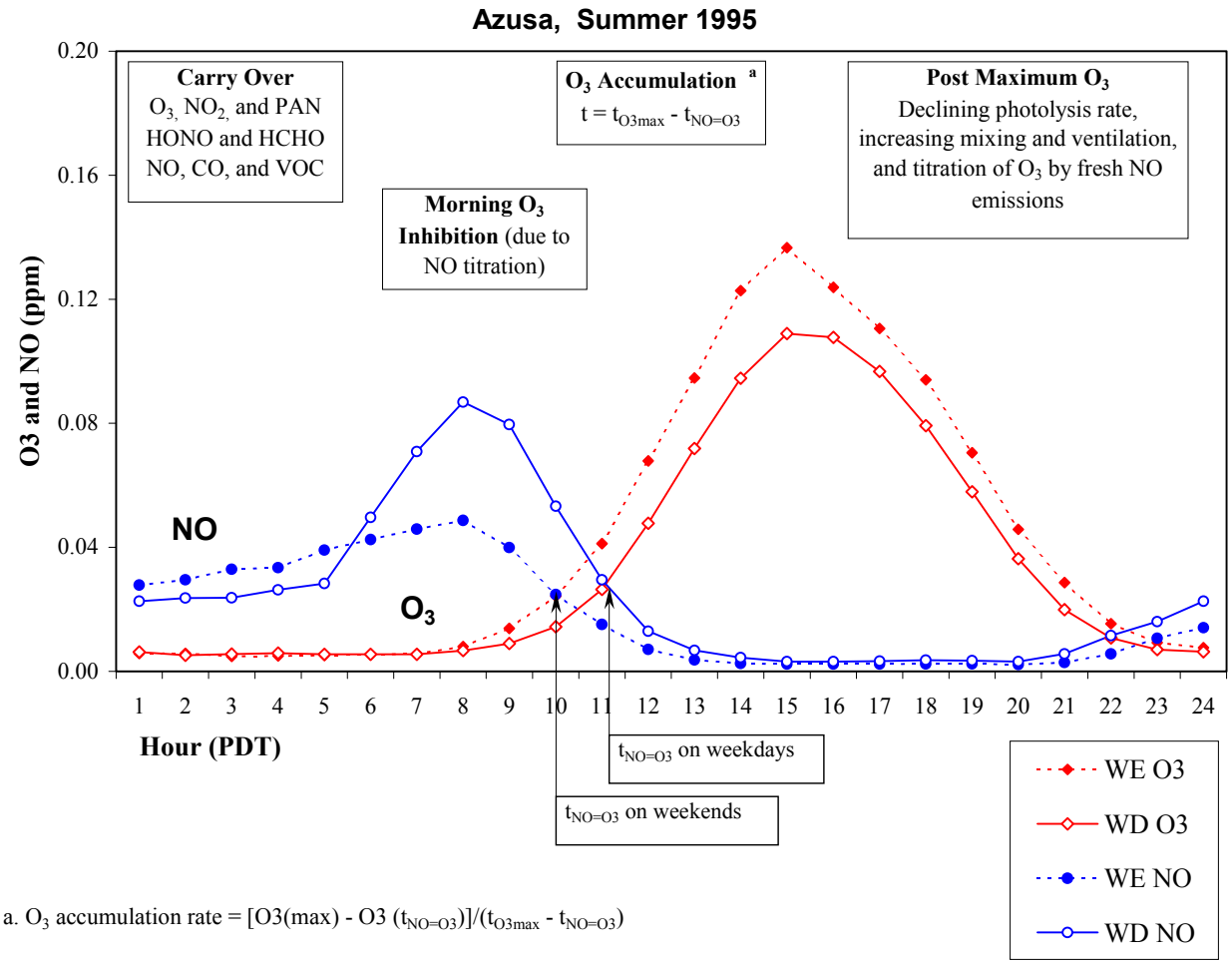

Figure 2-8. Average summer 1995 diurnal variations of ozone and nitric oxide at Azusa during the weekday and weekend. The shorter morning ozone inhibition period and higher rate of ozone accumulation are the main factors that result in higher ozone on weekends.

variations of O_3 and NO at Azusa for summer 1995. Lower NOx emissions on weekends decrease NO titration of the O_3 newly formed at the surface and the ozone transported from aloft.

The retrospective analysis of the ambient data showed that the intensity and spatial extent of the weekend ozone effect are associated with weekday-weekend differences in the degree of ozone inhibition and rate of ozone accumulation. Lower NO concentrations and higher NO_2/NOx ratios during weekend mornings decrease the removal of ozone by titration with NO, thereby allowing ozone to accumulate about an hour earlier on weekends compared to weekdays. This advance in timing of ozone accumulation on weekends is similar throughout the Basin, and it has remained relatively constant from 1981 to 1999. In contrast, the rate of ozone accumulation from the end of ozone inhibition to the time of ozone maximum decreased by one-half over the same

time period with largest reductions occurring in the central Basin. Rates of ozone accumulation were consistently lower on weekends than weekdays through most of the 1980s but became consistently higher on weekends during the 1990s. Central and eastern parts of the Basin showed either no change or slightly lower ozone concentrations on weekends (i.e., a small weekend effect) in the 1980s because the shorter ozone inhibition periods were offset by the lower rates of ozone accumulation. A switch to higher weekend ozone accumulation rates in the 1990s, coupled with a shorter inhibition period, resulted in higher weekend ozone concentrations during the 1990s and a strengthening of the weekend ozone effect within the Basin.

Under typical summer transport pattern in the Basin, less time is available near the coast for ozone to accumulate before ventilation occurs. The ozone accumulation period is about three hours near the coast and increases to about six hours in the eastern part of the Basin. During transport to the east side of the Basin, VOC/NOx ratios increase due to more rapid removal of NOx versus VOC resulting in increased rates of ozone formation. Addition of dispersed NOx sources in downwind suburban areas may extend the area of VOC limitation further downwind, and increases in the rate of ozone formation due to increasing VOC/NOx ratios during transport may be offset by dilution in the absence of fresh emissions. Near the coastline, the day-of-week differences in the VOC/NOx ratios have greater influence on weekday versus weekend differences in peak ozone concentrations due to the shorter time for ozone accumulation. In the eastern Basin, day-of-week differences in the initial VOC/NOx ratios and the resulting differences in O_3 formation rates have less effect on weekday versus weekend peak ozone concentrations because of the longer O_3 accumulation times, which allow ozone formation to proceed more to completion. Thus the weekend ozone effect reaches the maximum intensity in the central Basin due to the competing factors of O_3 accumulation time and rate of O_3 formation. Day-of-week differences in these air quality parameters arise from day-of-week changes in the spatial and temporal distribution of VOC and NOx emissions due to changes in activity patterns.

VOC/NOx ratios affect both the rate and efficiency of ozone production. Photochemical reactivity of the VOC mixture also affects the rate of ozone formation, but reactivity of the VOC is lower on weekends and does not account for the higher ozone formation rates on weekends. The weekend effect is greatest where the ozone formation is more VOC-limited during the weekday and less VOC-limited during the weekends. VOC/NOx ratios have decreased by one-half over the past 15 years. The increase in the VOC/NOx ratio on weekends due to decreased NO emissions is consistent with the observed evolution of the weekend effect in the SoCAB over the past two decades and current diurnal and day-of-week variations in ozone relative to VOC, NO and NO_2 concentrations and NO_2/NOx, VOC/NOx ratios. This transition parallels the downward trend in peak ozone levels, a shift in the location of peak ozone levels from the central portion of the Basin (e.g., Pasadena to Azusa) to the eastern portion of the Basin (e.g., Lake Gregory), and an increase in the magnitude and spatial extent of the weekend ozone effect in the SoCAB.

2.4 Key Findings Relevant to the Proposed Hypotheses for the Weekend Ozone Effect

The key findings and conclusions of our study are organized in this section according to each of the six hypotheses for the observed weekend ozone effect in the South Coast Air Basin. An up or down arrow preceding each finding indicates whether it supports (↑) or contradicts (↓)

the hypothesis. Inconclusive findings are indicated by a right arrow (→). Each finding is related to the section in Volumes II and/or III of the report where it is discussed.

Hypothesis #1 - NOx Reduction

According to this hypothesis, lower NOx concentrations on weekend mornings lead to higher ozone concentrations on weekends because: 1) ozone accumulation begins earlier on weekends due to lower NO emissions and therefore less titration of ozone with NO; and 2) there is a higher rate of ozone accumulation due to higher VOC/NOx ratios. The lower concentrations of NO and higher VOC/NOx ratios on weekend mornings are due lower motor vehicle activity, especially heavy-duty diesel truck (and bus, train). VOC emissions from LDGVs are also reduced on weekends, but total reductions in mobile source NOx emissions exceed reductions in VOC emissions resulting in higher VOC/NOx ratios.

↑ Average 7-8 a.m. NO concentrations on Saturday and Sunday are 55-70 percent and 33-39 percent lower than average weekday concentrations, respectively. The average NO_2/NOx ratios at 7-8 a.m. (PDT) are about 0.4 on weekdays, about 0.5 on Saturday and close to 0.6 on Sunday. The ozone accumulation starts 0.5 to 0.7 hour earlier on Saturdays and about 1.1 to 1.3 hours earlier on Sundays. In general, ozone inhibition ends earlier in downwind areas and later in areas of highest amounts of fresh NO emissions. The delay in the start of ozone accumulation due to inhibition on weekdays relative to weekends has changed very little in 18 years. (Vol. II, Section 2.4)

↑ The decrease of ozone precursor concentrations on weekends is proportionately greater for NO than NMHC for all times of the day resulting in higher weekend NMHC/NOx ratios. Trends in concentrations of ozone precursors over the past 20 years show a transition in the SoCAB to lower VOC/NOx ratios in much of the Basin and greater differences between weekday and weekend VOC/NOx ratios (higher weekend ratios relative to weekday). The ratios of the average 6-9 a.m. NMHC/NOx ratio (NMHC estimated from CO) on Saturday to that on Wednesday were 1.05, 1.06, 1.17, and 1.18 for the years 1981-84, 1985-89, 1990-94, and 1995-98, respectively. The corresponding Sunday/Wednesday ratios are 1.10, 1.17, 1.27 and 1.42. (Vol. II, Section 2.6)

↑ Current (1999-2000) NMHC/NOx ratios in the SoCAB are about half the ratios observed during the 1987 Southern California Air Quality Study. This decrease is due primarily to reductions in hydrocarbon emissions. The mean NMHC/NOx ratios (mean of PAMS NMHC data from Los Angeles North Main, Pico Rivera, Azusa, and Upland) during 0600-0900 ranged from 31 to 59 percent higher on Sunday (mean of 46 percent) and 20 to 39 percent higher on Saturday (mean of 29 percent). The mean 0600-0900 NMHC/NOx ratios (ppbC/ppbv) are 4.9 and 5.5 on Saturday and Sunday, respectively and increase to a high of 6.7 and 7.5 during the period of peak ozone (1200-1500). The mean NMHC/NOx ratio is 4.6 on Monday and ranges from 3.7 to 3.9 for other weekdays. The mean midday NMHC/NOx ratios do not exceed seven. Ozone formation is VOC-limited throughout the day at all the sites examined. (Vol. II, Section 3.2)

- Ozone accumulation rates were cut in half during 1981 to 1998 with the largest reductions in the central Basin. These changes are consistent with changes in VOC/NOx ratios during this period. (Vol. II, Section 2.5 and 3.2)

- During the past twenty years (1980 to 2000), peak ozone concentrations at Azusa have steadily decreased relative to its maximum potential (sum of O_3 and NOx) on weekdays. In contrast, peak ozone concentrations on Sundays have remained constant relative to its maximum potential. The ratios of peak to potential ozone on Saturdays were similar to Sundays during the 1980s through mid-1990s, but have since decreased. (Vol. II, Section 3.4)

- Combining emission changes for all categories (including off-road categories) by day of week results in an estimate that daily total 2000 ROG and NOx emissions in the SoCAB on weekends in the summer decrease by about 12 to 18% and 35 to 41% on Saturdays and Sundays, respectively, relative to weekdays. These changes in emissions result in an increase of the ROG to NOx ratio of more than 30% on weekends. During the morning hours between 6 a.m. and 9 a.m. NOx emissions decrease 49% from weekdays to Saturday and 52% from weekdays to Sunday. (Vol. III, Section 2.4)

- In the urban areas of the SoCAB, surface street traffic volumes (which were dominated by light-duty vehicles) are reduced by about 15% to 30% on weekends and tended to peak around midday rather than during the weekday a.m. and p.m. rush hours. In addition, traffic volumes are delayed about one hour on Sundays compared to Saturdays. (Vol. III, Section 2.3)

- Freeway traffic volume information showed that truck and bus activities decreased by up to 80%. On weekends in areas just beyond the urban zones, daily traffic volumes increased somewhat on weekends and tended to peak on Friday and Sunday late afternoons. (Vol. III, Section 2.3)

- In the year 2000, the one of the largest contributors to emission changes on the weekends is a substantial decline in heavy-duty truck traffic (representing 25% of all NO_x emissions on weekdays and 12 to 15% of all NO_x emissions on weekends). Other source categories with large reductions in NOx emissions on weekends include: construction equipment and other off-road engines such as locomotives. (Vol. III, Section 2.4)

- The ambient concentrations of NO and black carbon are well correlated and exhibit similar diurnal and spatial variations, and weekday/weekend differences. CO and VOC have temporal and spatial variations that are similar to each other, but they differed significantly from those exhibited by NOx and black carbon. The contribution of gasoline-powered vehicles to ambient NOx on a typical Saturday during the ozone accumulation period (9 a.m. to noon) is comparable to their contribution on weekdays. The contribution of gasoline-powered vehicles to ambient NOx is about 25 percent lower on Sunday compared to weekdays. In contrast, the contributions of diesel vehicles during the ozone accumulation period to ambient NOx on Saturday and Sunday are about one-half and one-third of its weekday contribution, respectively. From the multiple regression analysis, the attributions of gasoline-powered vehicles to on-road emissions of NOx

during the 9 a.m. to noon period are 45, 57 and 66 percent for weekday, Saturday, and Sunday, respectively. (Vol. II, Section 4.3, and 4.5)

- ↑ Gasoline exhaust is the predominant source of nonmethane hydrocarbons (NMHC) in all samples ranging from 60-80% for on-road samples and samples taken at more regionally representative locations. The diurnal and weekday/weekend variations in the relative contributions of NMHC are more variable for diesel exhaust than gasoline exhaust. The relative contributions of diesel exhaust are greatest during the weekday on freeway loops with the greatest fraction of diesel traffic. Diesel exhaust contributed 20 percent of NMHC on the Pomona Loop on Monday, October 2, compared to only 3 percent on Sunday, October 8. The same percentages are 18 and 6 percent on Wednesday, October 4 and Saturday, October 7. Day-of-week changes in the contributions of diesel exhaust to ambient NMHC have much less impact on NMHC/NOx ratios than day-of-week changes in the contribution of diesel exhaust to ambient NOx concentrations. (Vol. II, Section 4.4)

- ↑ VOC/NOx (ppbC of VOC to ppb of NOx) ratios on freeways ranged from 0.5 to 2. The light-duty gasoline-powered vehicle fleet, as represented by the freeway samples without diesel truck traffic, has an average VOC/NOx ratio of about 3.5. This value is similar to the VOC/NOx ratios measured at Industry Hills and Dodger Stadium. VOC/NOx ratios at Azusa are consistently about five during the weekdays with little diurnal variation. Ratios were greater during the weekends, ranging between 5 and 10. (Vol. II, Section 4.3)

- ↑ Major point source NOx emissions on Friday, Saturday, and Sunday were 8% to 18% lower, on average, than on Monday through Thursday. (Vol. III, Section 2.3)

- ↑ Weekday/weekend off-road emissions were modeled using lawn and garden and business internal combustion (IC) engine activity data. These off-road? 2000 ROG and NO_x emissions in the summer decline on weekends by 41 to 64% and 72 to 78% on Saturdays and Sundays, respectively, relative to weekdays. Note that day-of-week patterns of off-road engine use, other than lawn and garden equipment, are uncertain because the limited data collected during the business portion of the survey may not represent the proper distribution of off-road IC engines. (Vol. III, Section 2.3)

Hypothesis #2 - NOx Timing

NOx emitted later in the morning on weekends into an aged photochemical system causes these emissions to produce ozone more efficiently compared to the NOx emitted on weekdays. The NOx timing hypothesis is applicable for NOx-limited conditions since increases in NO emissions under VOC-limited conditions will initially decrease ozone production.

- ↑ In urban areas, light-duty vehicle traffic peaks around midday on weekends rather than during the morning and afternoon rush hours. (Vol. III, Section 2.3) In addition, traffic volumes are delayed about one hour on Sundays compared to Saturday.

- ↓ Observed NMHC/NOx ratios range from 4-8 from sunrise to peak ozone and ozone formation is VOC-limited throughout this period. Expectation of the NOx timing

hypothesis is that ozone formation is NOx-limited on weekend mornings. (Vol. II, Section 3.2)

↓ Weekday-weekend differences in the diurnal pattern of NO and ozone are established early in the morning and remain a constant multiplicative constant throughout the daylight hours. These results are counter to the expectations of the NOx timing hypothesis, which requires a proportional increase in NO and O_3 mixing ratios on weekends later in the morning compared to weekdays. (Vol. II, Section 3.4)

↓ The weekday-weekend differences in the timing of motor vehicle emissions does not explain the decrease in peak ozone relative to its maximum potential ozone on weekdays or the greater decrease in ozone accumulation rates on weekdays during the past two decades. (Vol. II, Section 3.6)

Hypothesis #3 - Pollutant Carryover Near the Ground

Greater carryover of precursor emissions due to different vehicle activity on Friday and Saturday evening results in an increased rate of ozone formation on weekend mornings.

↑ Light-duty vehicle traffic on Friday and Saturday nights is about 25% higher than on weekday nights and vehicle traffic on Sunday nights is about 15% higher than on weekday nights. (Vol. III, Section 2.3)

↑ Carryover of NMHC concentration is about 10 to 20 percent higher on weekend mornings relative to midweek. Carryover of NO is 10 to 20 percent lower on Sunday and Monday mornings relative to midweek. (Vol. II, Section 2.3)

→ The effect of weekday differences in precursor concentrations during the carryover period on NMHC/NOx ratios during the ozone accumulation period is small. (Vol. II, Section 2.3)

Hypothesis #4 - Pollutant Carryover Aloft

Carryover of aged pollutants from aloft on weekends has greater influence on weekend mornings due to lower emissions of NOx.

↓ Mixing occurs about 9 a.m. SCAQS and SCOS meteorology data show that contribution is small. (STI Phase I report, Vol. III, Section 3.5, 3.6)

↓ Pollutant concentrations aloft are significantly lower than in the past. This is inconsistent with strengthening of the weekend ozone effect in the 1990s. (STI Phase I report, Vol. III, Section 3.5, 3.6)

↓ Weekday-weekend differences in the diurnal pattern of NO and ozone are established early in the morning and remains a constant multiplicative constant throughout the daylight hours. (Vol. II, Section 3.4)

Hypothesis #5 - Increased Weekend VOC Emissions

Increased VOC emissions from use of lawn and garden equipment, recreational vehicles, backyard barbecues, and household solvents on weekends result in higher weekend ozone concentrations.

↓ A survey of business activity showed that business activity, including commercial lawn and garden landscaping operations, declined substantially on weekends (by up to 80%). The observed decrease in weekend commercial lawn and garden operations more than offsets the increased residential lawn and garden activity given in the next finding. (Vol. III, Section 2.3)

→ A survey of residential activity showed that while some residential activity increased substantially on weekends, (primarily lawn and garden and barbecues use) most residential activity was independent of day of week. (Vol. III, Section 2.3)

↓ Ambient apportionments of non-mobile sources to ambient NMHC do not show significant day-of-the-week variations, and they have little effect on weekday variations in VOC/NOx ratios. (Vol. II, Section 4.4)

Hypothesis #6 - Increased Photolysis Due to Decreased Emissions of Fine Particles

Lower PM concentrations during weekends increase radiation available for photolysis, thus increasing the rate of ozone formation compared to weekdays.

↑ Photolysis rate parameters have increased historically. The photolysis rate parameter for NO_2 (J_{NO2}), estimated from an extended version of the O_3-NO-NO_2 photostationary state expression, increased over the period from 1980 to 2000 This is consistent with the trend to lower soot emissions. (Vol. II, Section 3.6)

↓ There are no significant weekend/weekday differences in photolysis rate parameters for the entire period from 1980 to 2000. (Vol. II, Section 3.6)

↓ Historically the proportion of ozone to potential ozone has not changed on Sundays, but has decreased on weekdays. This is contrary to the historic increase in photolysis rate parameters. (Vol. II, Section 3.6)

3. CONCLUSIONS AND IMPLICATIONS

Based upon the findings in the previous section, we conclude whether the hypothesized explanations have a significant effect, a moderate or contributing effect, or an insignificant effect on the observed weekday variations in ozone concentrations. The conclusions are summarized in Table 3-1. Each conclusion is assigned a level of confidence according to the following criteria:

- High confidence: There is high certainty in the data or data analysis approach or the conclusion is supported by more than one independent analysis approach, each of which has low to moderate uncertainties.

- Medium confidence: There is moderate uncertainty in the data or data analysis approach and independent analysis approaches were not applied.

- Low confidence: There is large uncertainty in the data or data analysis approach and independent analysis approaches were not applied or were contradictory.

Table 3-1
Significance of Proposed Hypotheses for the Weekend Ozone Effect in the South Coast Air Basin

Hypotheses	Significance for Ozone Formation	Confidence Level
1. NOx reduction	Significant	High
2. NOx timing	Insignificant *	High
3. Pollutant carryover near the ground	Small	High
4. Pollutant carryover from aloft	Insignificant	Medium
5. Increased weekend VOC emissions	Small to Insignificant	Medium
6. Increased photolysis due to decreased PM	Small to Insignificant	Medium

* May be applicable in areas where ozone formation is NOx limited.

The evolution of the weekend ozone effect in the SoCAB over the past twenty years is rooted in the chemistry of ozone formation in that differences in the efficiency and rate of ozone production cause the variations between weekdays and weekends. These differences arise from day-of-week differences in the temporal and spatial patterns of VOC and NOx emissions. Based

upon our results, we conclude that the NOx reduction hypothesis (#1) is most consistent with spatial and temporal variations in available ambient air quality and emission activity data and long-term trends in the magnitude and spatial extent of the weekend ozone effect. The fundamentals of ozone photochemistry impose two necessary conditions for a reduction in NOx on the weekend to result in higher production of ozone. The first condition is that ozone formation be VOC-limited. Removing NOx from a VOC-limited system increases the efficiency and rate of ozone formation by reducing the removal of HO radical by reaction with NO_2 to form nitric acid. The weekend effect is greatest where the ozone formation is more VOC-limited during weekdays and less VOC-limited during the weekends. The evolution in the magnitude and spatial extent of the ozone effect over the past twenty years is consistent with greater reduction in VOC concentrations relative to NOx and higher weekend VOC/NOx ratios. The second condition is that the peak ozone level on weekdays does not reach its maximum potential and time is a limiting factor in ozone production. Analysis of the ambient air quality trends shows that this is the case in the SoCAB. Consequently, peak ozone is determined by the duration of ozone accumulation, which is a function of the extent of ozone inhibition due to NO emissions, and rate of ozone accumulation, which depends on the VOC/NOx ratio. Although the amount of ozone that can potentially form on weekdays is greater, peak ozone levels are higher on weekends because the duration of ozone accumulation is longer and the rate of ozone formation is greater on weekends.

The study findings are counter to the expectations of the NOx timing hypothesis (#2). During the summers of 1999 and 2000, the NMHC/NOx ratios at the four SoCAB PAMS sites were in the range of four to eight from sunrise to the time of peak ozone so that ozone formation is VOC-limited throughout this period. Blanchard and Tanenbaum (2000) concluded based on estimates of the extent of reaction that most monitoring sites in the SoCAB are VOC-limited. Increases in NO emissions under VOC-limited conditions will initially decrease ozone production and lead to increased ozone in downwind areas only after the chemical system has transitioned to NOx-limited conditions. The other four hypotheses have an insignificant to small overall influence on the explaining elevated weekend ozone levels in the SoCAB.

Theoretical analysis in Figures 3-1 and 3-2 shows why VOC control measures undertaken between 1987 and 2000 have been effective in reducing ozone. The ozone isopleth diagram derived from the Empirical Kinetics Modeling Approach (EKMA) predicts that ozone concentrations should have reduced ozone concentrations from 200 ppb to an average near 100 ppb during this period, which is in reasonable agreement with observations. The current concentrations of VOC and NOx are in the VOC-limited portion of the EKMA diagram for both weekends and weekdays. The diagram shows that the decrease in NOx leads to an increase in ozone concentrations of about 40 ppb between weekdays and weekends, and this is consistent with observations. The EKMA analysis shows that that an ozone disbenefit will result if NOx emissions are decreased at current levels of VOC until the NOx mixing ratios are decreased by roughly 90 percent to about 10 to 12 ppb where ozone production becomes NOx-limited. The indicator ratios for photochemical activity on the EKMA diagrams, including $[HNO_3]/[H_2O_2]$ and $[H_2O_2]/[HCHO]$, show that ozone production is VOC-limited for current NOx and VOC mixing ratios.

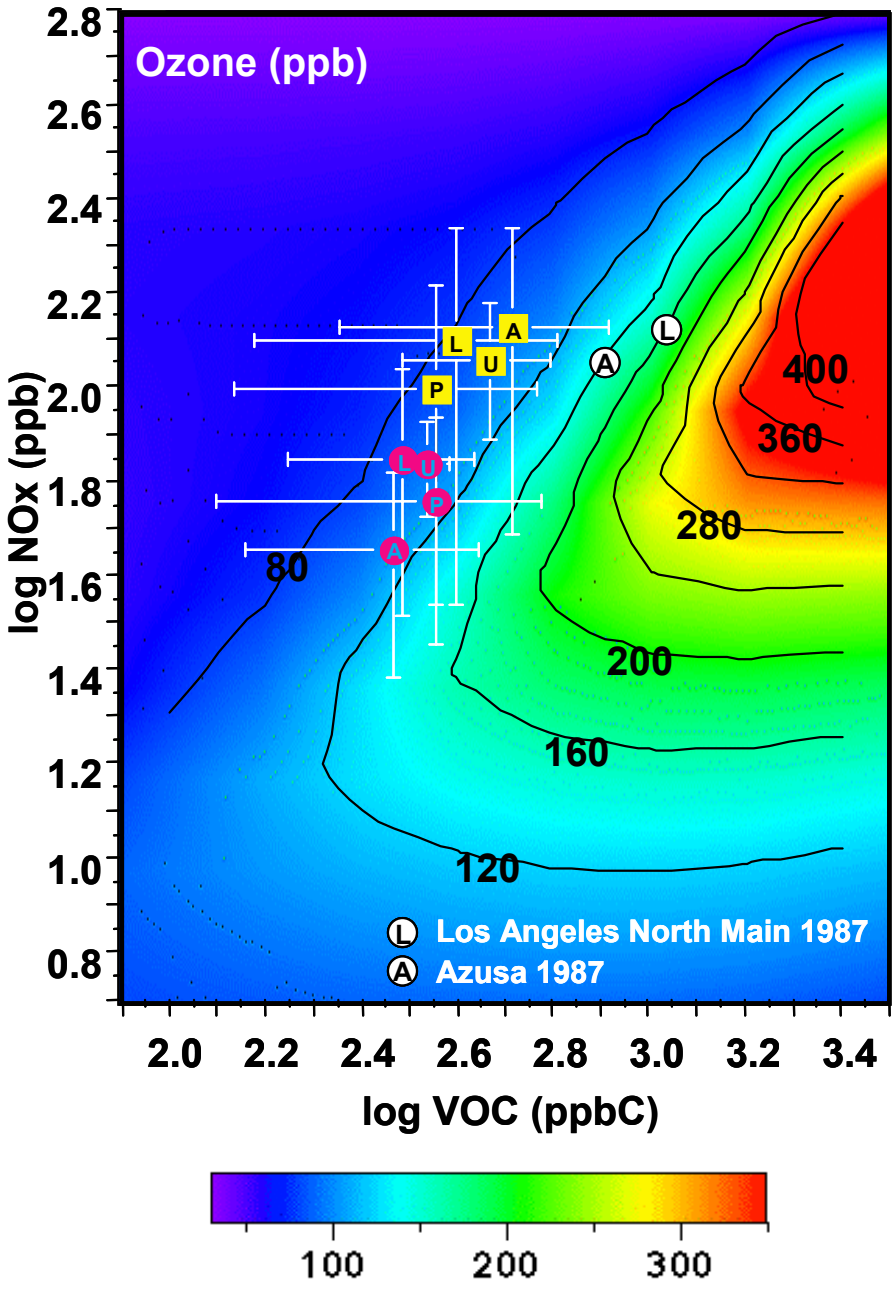

Figure 3-1. Ozone EKMA plot. Mixing ratios for NOx and NMHC during the summer of 1999 and 2000 with error bars representing one standard deviation from the average with the labels (A) representing Azusa, (L) representing Los Angeles-North Main, (P) representing Pico and (U) representing Upland. The yellow squares represent Wednesday and the dark red dots represent Sunday. The error bars are not symmetrical because of the logarithmic scale. The two white dots labeled (L) and (A) represent the average conditions for Los Angeles-North Main and Azusa during 1987, respectively. The simulation conditions are given in Chapter 3 of this report.

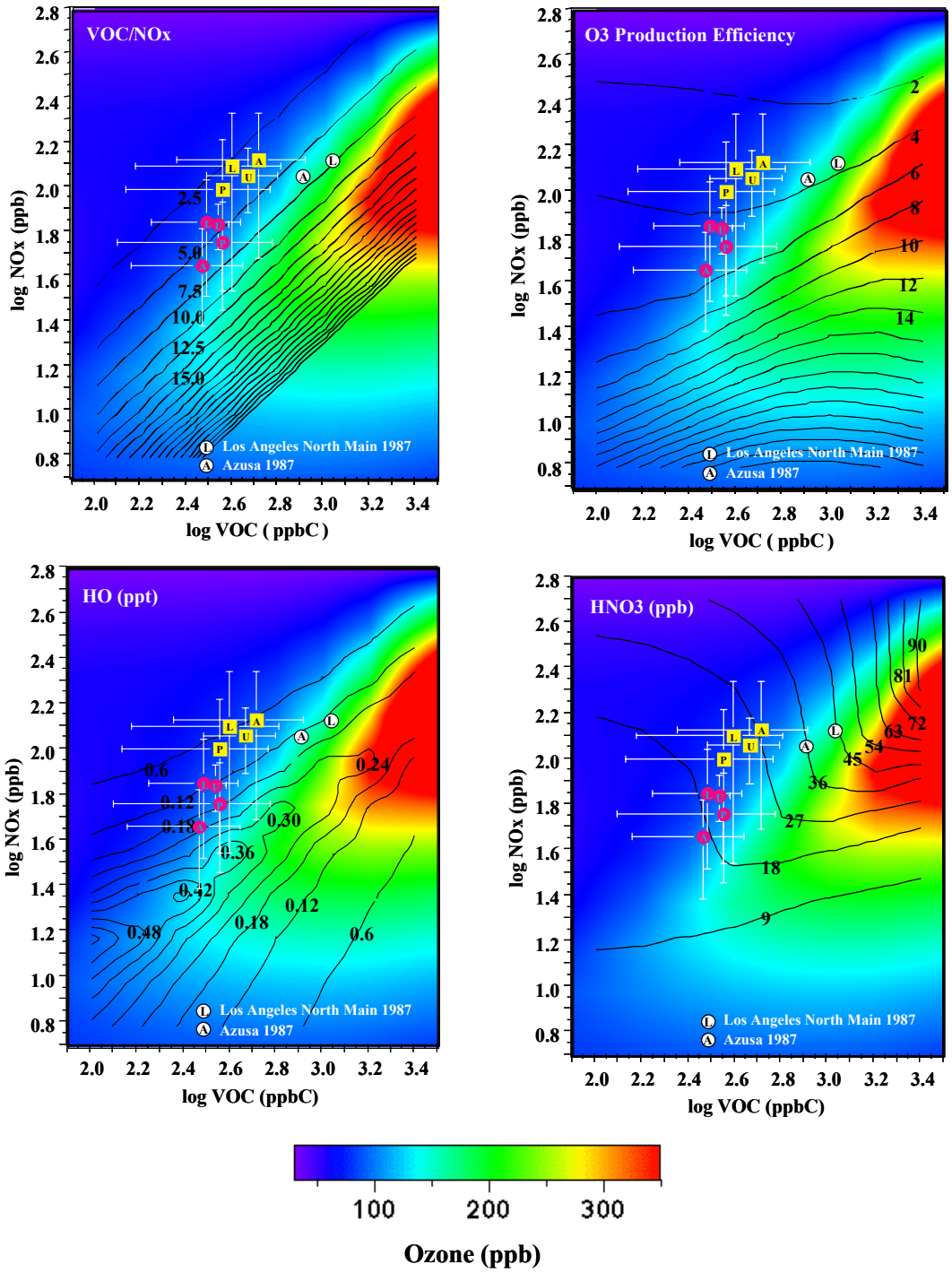

Figure 3-2 Plots of VOC/NO_x ratio, ozone production efficiency ($\Delta[O_3]/(\Delta[HNO_3]$ + Δ[Organic Nitrates]), hydroxyl radical, and nitric acid superimposed on a color O_3 EKMA plot.. Also plotted are mixing ratios for NO_x and NMHC during the summer of 1999 and 2000 with error bars representing one standard deviation from the average with the labels (A) representing Azusa, (L) representing Los Angeles–North Main, (P) representing Pico Rivera and (U) representing Upland. The yellow squares represent Wednesday and the dark red dots represent Sunday. The error bars are not symmetrical because of the logarithmic scale. The two white dots labeled (L) and (A) represent the average conditions for Los Angeles–North Main and Azusa during 1987, respectively.

The VOC/NOx ratio decreased from near an average of 7.5 during 1987 to between 3 and 5 during 1999-2000. On weekends, the VOC/NOx ratio increases to between 4 and 7, and it may reach 10 or 12. The simulations show that the shift in VOC/NO_x ratio increases the average ozone production efficiency from less than 4 to between 4 and 6. The simulations also show that hydroxyl radical mixing ratios increase with decreasing NOx concentrations. Daytime nitric acid production has decreased between 1987 and 2000 due to the decrease in VOC mixing ratios. Current production of HNO_3 is expected to be lower by about 9 ppb between weekends and weekdays. PAN, HCHO, aldehyde and organic nitrates have been reduced due to reductions in VOC concentrations, but their concentrations are not strongly affected by the NOx at current concentrations so a weekend effect is not expected for these species.

Although projecting emission inventories into the future is quite uncertain, application of the day-of-week patterns developed in this study to published projected emissions permit us to speculate on future-year emissions ratios and future-year ozone concentrations by day-of-week. For example, using emission forecasts by the CARB for 2010 results in a prediction of ozone precursor emissions on weekdays in 2010 comparable to those on weekends in 2000 (see Figure 3-3**).** The forecast of higher ratios in 2010 suggests that weekday and weekend ozone concentrations could be even higher in future years unless the levels of NO_x control are large enough to change the atmosphere in the SoCAB to a NO_x-limited regime. Continuing the analysis, the forecast emissions by day-of-week can be used to forecast ROG-to-NO_x emissions molar ratios. Figure 3-4 shows the forecast ratios for 2010 for the SoCAB. As in year 2000, ROG/NO_x ratios increase on the weekends. Application of day-of-week patterns to future-year published emission inventories suggests that because of predicted increases of the ROG/NO_x ratio in emissions, ozone concentrations in the future may not decline despite predicted decreases in emissions.

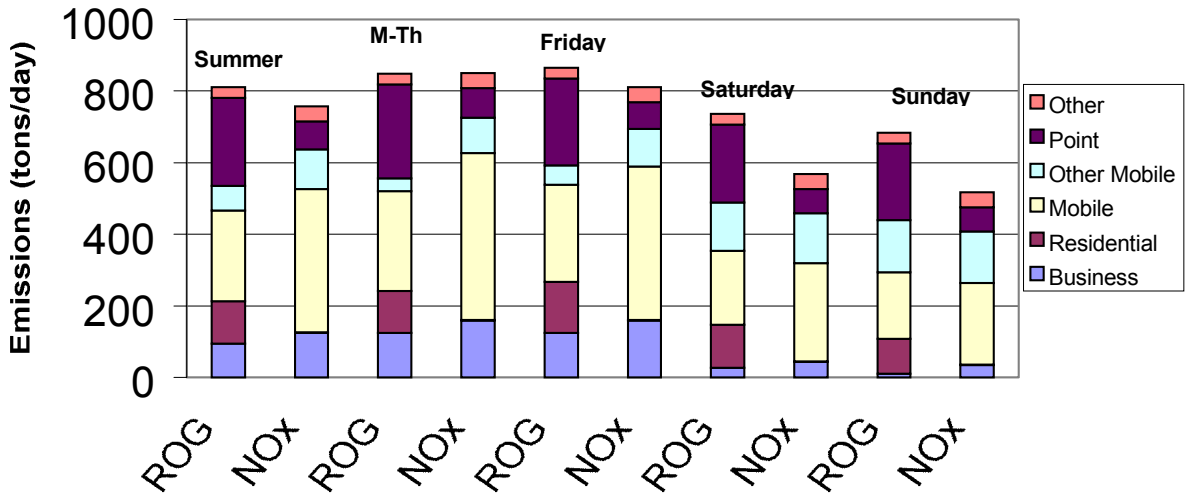

Figure 3-3. Predicted 2010 day-of-week emissions in the SoCAB.

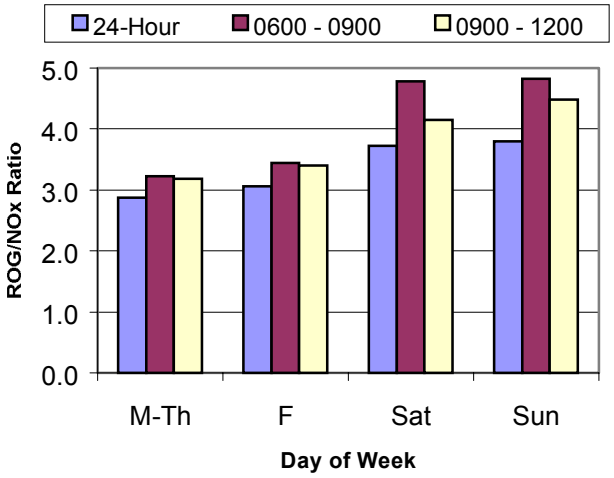

Figure 3-4. Predicted 2010 ROG/NO_x molar emissions ratios for the SoCAB.

4. RECOMMENDATIONS FOR FUTURE WORK

The varying emissions that occur between weekday and weekend periods allow us to understand how ozone concentrations change in response to decreases in ozone precursor emissions, and also provide a natural test of the ability of air quality simulation models to simulate accurately weekday-weekend differences in ozone and its precursors. One of the most important applications of this test is that it helps to probe the relative sensitivity of ozone concentrations to VOC and NOx. The Coordinating Research Council is sponsoring a study by ENVIRON to conduct proximate modeling of weekday/weekend ozone episodes in the SoCAB using input data collected during the SCOS97-NARSTO field study to determine whether proposed hypotheses explain the weekend ozone effect. Similar modeling is planned by the ARB after developing a weekend emissions inventory for SoCAB.

The results of our study show that there are substantial variations in emissions by both day-of-week and by location within the SoCAB. The impact of both the spatial and temporal variations in emissions on ozone concentrations should be better quantified. Only through the development of accurate temporally and spatially resolved day-of-week emissions inventories used as inputs to photochemical models can the impacts be better quantified.

We recommend the following evaluations of the modeling performance and corroborative data analysis and air quality monitoring.

1. Compare modeling results against the measured temporal and spatial variations of ozone and ozone precursors.

2. Perform a series of modeling runs using realistic, alternative future emissions inventories for 5, 10 and 15 years into the future and assess direction and sensitivity of projected concentrations of ozone, PAN, nitric acid, particulate nitrate, and formaldehyde.

3. Assess changes in downwind areas where emissions transported from the SoCAB could transition from VOC limited to NOx-limited. With continued growth downwind of the SoCAB, these previously downwind areas' air quality will tend to look like fresh emissions. Also, if VOC emissions in the source regions are efficiently controlled, evaluate how much ozone would be reduced in the downwind regions.

4. Assess relative changes to maximum 1-hour and 8-hour ozone levels within the Basin.

5. Measure species such NOy, PAN, HCHO, H_2O_2, and speciated hydrocarbons in downwind area to provide corroboration of modeling results.

6. Reconcile the effects of different reaction mechanisms on day-of-week variations in predicted ozone concentrations.

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